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(54) Title: COMPOSITIONS COMPRISING DIFLUOROPROPENE AND USES THEREOF

(57) Abstract: The present disclosure relates to compositions comprising HFO-1252zc, HFC-32, and HFO-1234zeE. The compositions are useful in methods of heating and cooling, air-conditioning and heat pump systems, and methods of replacing existing refrigerants.

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TITLE OF THE INVENTION

COMPOSITIONS COMPRISING DIFLUOROPROPENE AND USES THEREOF

FIELD

[0001] The present disclosure relates to compositions useful as refrigerants, and in particular, for air-conditioning and heat pump systems. The compositions of the present disclosure are useful in methods for producing cooling and heating, and methods for replacing refrigerants and air-conditioning and heat pump systems.

BACKGROUND

[0002] The fluorocarbon industry has been working for the past few decades to find replacement refrigerants for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) being phased out as a result of the Montreal Protocol. The solution for many applications has been the commercialization of hydrofluorocarbon (HFC) compounds for use as refrigerants, solvents, fire extinguishing agents, blowing agents and propellants. These new compounds, such as HFC refrigerants, HFC-134a and HFC-125 being the most widely used at this time, have zero ozone depletion potential (ODP) and thus are not affected by the current regulatory phase-out as a result of the Montreal Protocol. In addition to ozone depleting concerns, global warming is another environmental concern in many of these applications. HFC refrigerants such as HFC-134a and HFC-125 respectively have global warming potentials (GWP) of 1,430 and 3,500 according to the UN's IPCC Fourth Assessment Report (AR4).

[0003] This regulatory landscape is continuously evolving, taking into consideration properties beyond just ODP and GWP. More particularly, there is a need for refrigerant compositions that not only meet low ODP standards and have low global warming potentials, but that also provide superior performance in a variety of applications, and which meet the standards of evolving regulations.

[0004] The present invention solves certain problems associated with conventional refrigerants and provides refrigerant blends containing 1,1-difluoropropene, which meet the evolving regulatory landscape.

SUMMARY

[0005] In order to meet the rapidly changing regulatory environment, the present inventors have identified a fluoroolefin compound that provides performance relative to existing refrigerants that will allow its use going forward even in view of the standards of the evolving regulatory landscape.

[0006] Certain embodiments disclosed herein relate to a fluoropropene composition comprising 1,1-difluoropropene (also called HFO-1252zc, or R-1252zc). This compound is shown herein to have advantageous properties for its use in refrigerant applications, such as air-conditioning and heat pumps.

[0007] In one embodiment, disclosed herein are compositions comprising HFO-1252zc, HFC-32, and HFO-1234zeE.

[0008] According to any of the foregoing embodiments, also disclosed herein are compositions comprising from about 0.5 to 65 weight percent HFO-1252zc, from about 1 to 22 weight percent HFC-32, and from about 13 to 78 weight percent HFO-1234zeE.

[0009] According to any of the foregoing embodiments, also disclosed herein are compositions comprising from about 1 to 65 weight percent HFO-1252zc, from about 21 to 22 weight percent HFC-32, and from about 13 to 78 weight percent HFO-1234zeE.

[0010] According to any of the foregoing embodiments, also disclosed herein are compositions comprising about 30 weight percent HFO-1252zc, about 21 weight percent HFC-32, and about 49 weight percent HFO-1234zeE

[0011] According to any of the foregoing embodiments, also disclosed herein are compositions further comprising at least one additional compound selected from HCFC-22, HFC-23, HCC-30, HCFC-31, HCC-40, HFC-41, methane, HFC-125, HFC-143, HFC-143a, HFC-152a, HFC-245cb, HCFC-253dc, HFC-254fb, HCC-260fb, HCFC-261fc, HCFC-262fc, HFC-263fb, HFC-272fb, propane, HFO-374, n-butane, allene, 2-butene, cyclobutene, 2-methyl propene, HCFO-1122, HFO-1132, HFO-1132a, HFO-1141, ethylene, HCFO-1233xf, HFO-1234yf, HCFO-1242zf, HFO-1243zf, HCFO-1251, HCO-1260zf, HFO-1261zf, propylene, HFO-1345, HFO-1252ze, HFO-1252yf, HFO-1252zf, HFO-1252ye, and E/Z-t-BuO-CF=CH-CH_3.

[0012] According to any of the foregoing embodiments, also disclosed herein are compositions further comprising at least one additional compound selected from HFO-1234yf, HFO-1243zf, HFC-263fb, HFO-1252ze, HFO-1252yf, HFO-1252zf, and HFO-1252ye.

[0013] According to any of the foregoing embodiments, also disclosed herein are compositions wherein said composition further comprises from 0.1 to 200 ppm by weight of water; from about 10 ppm by volume to about 0.35 volume percent oxygen; and/or from about 100 ppm by volume to about 1.5 volume percent air or NAG.

[0014] According to any of the foregoing embodiments, also disclosed herein are compositions wherein said composition comprises a stabilizer.

[0015] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein the stabilizer is selected from the group consisting of nitromethane, ascorbic acid, terephthalic acid, azoles, phenolic compounds, cyclic monoterpenes, terpenes, phosphites, phosphates, phosphonates, thiols, and lactones.

[0016] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein the stabilizer is selected from tolutriazole, benzotriazole, tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-terbutyl-4-methylphenol, fluorinated epoxides, n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, d-limonene, α-terpinene, β-terpinene, α-pinene, β-pinene, or butylated hydroxytoluene.

[0017] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein the stabilizer is present in an amount from about 0.001 to 1.0 weight percent based on the weight of the refrigerant.

[0018] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein the composition further comprises a lubricant.

[0019] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein said lubricant is at least one selected from the group consisting of polyalkylene glycol, polyol ester, poly-α-olefin, and polyvinyl ether.

[0020] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein said lubricant is a polyol ester or a polyvinyl ether.

[0021] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein said lubricant has at least one property selected from the group consisting of volume resistivity of greater than 10^{10} Ω-m at 20 ºC; surface tension of from about 0.02 N/m to 0.04 N/m at 20 ºC; kinematic viscosity of from about 20 cSt to about 500 cSt at 40 ºC; a breakdown voltage of at least 25 kV; and a hydroxy value of at most 0.1 mg KOH/g.

[0022] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein the composition comprises at least one tracer.

[0023] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein said tracer is present in an amount from about 1.0 ppm by weight to about 1000 ppm by weight.

[0024] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein said at least one tracer is selected from the group consisting of hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof.

[0025] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein said at least one tracer is selected from the group consisting of HFC-23, HCFC-31, HFC-41, HFC-161, HFC-143a, HFC-134a, HFC-125, HFC-236fa, HFC-236ea, HFC-245cb, HFC-245fa, HFC-254eb, HFC-263fb, HFC-272ca, HFC-281ea, HFC-281fa, HFC-329p, HFC-329mmz, HFC338mf, HFC-338pcc, CFC-12, CFC-11, CFC-114, CFC-114a, HCFC-22, HCFC-123, HCFC-124, HCFC-124a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-244bb, HCC-40, HFO-1141, HCFO-1130, HCFO-1130a, HCFO-1131, HCFO-1122, HFO-1123, HFO-1234yf, HFO-1234ye, HFO-1243zf, HFO-1225ye, HFO-1225zc, PFC-116, PFC-C216, PFC-218, PFC-C318, PFC-1216, PFC-31-10mc, PFC-31-10my, and combinations thereof.

[0026] According to any of the foregoing embodiments, also disclosed herein are compositions, wherein the composition is free of or substantially free of Group A

Fluorinated Substances, and wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.

[0027] According to any of the foregoing embodiments, also disclosed herein are methods for cooling comprising evaporating the composition in the vicinity of a body to be cooled and thereafter condensing said composition, wherein said cooling is provided by an air-conditioner or heat pump.

[0028] According to any of the foregoing embodiments, also disclosed herein are methods for heating comprising evaporating the composition and thereafter condensing said composition in the vicinity of a body to be heated, wherein said heating is provided by a heat pump.

[0029] According to any of the foregoing embodiments, also disclosed herein are systems for cooling or heating comprising the composition. In another embodiment, the systems comprise an evaporator, compressor, condenser, and expansion device, each operably connected to perform a vapor compression cycle. In another embodiment, said air-conditioner or heat pump is a residential, light commercial, or industrial air-conditioner or heat pump. In another embodiment, the system may be a secondary loop system.

DETAILED DESCRIPTION

[0030] This invention relates to compositions containing 1,1-difluoropropene (HFO-1252zc), difluoromethane (HFC-32), and E-1,3,3,3-tetrafluoropropene (HFO-1234zeE). The compositions may potentially be candidates to replace refrigerants such as R-454C, R-410A, or propane with low Global Warming Potential (GWP), improved environmental fate characteristics, and improved energy efficiency (COP).

[0031] The compositions comprise HFO-1252zc, HFC-32, and HFO-1234zeE. They provide refrigerant blends with low global warming potential, improved glide as compared to other suggested refrigerant blends, and improved coefficient of performance as compared to existing refrigerants and other proposed replacements.

[0032] A refrigerant is defined as a heat transfer fluid that undergoes a phase change from liquid to gas and back again during a cycle used to transfer of heat.

[0033] A heat transfer system is the system (or apparatus) used to produce a heating or cooling effect in a particular space. A heat transfer system may be a mobile system or a stationary system.

[0034] Examples of heat transfer systems are any type of refrigeration systems and air conditioning systems including, but are not limited to, stationary heat transfer systems, air conditioners, freezers, refrigerators, heat pumps, flooded evaporator heat pumps, direct expansion chillers heat pumps, chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, mobile refrigerators, mobile heat transfer systems, mobile heat pumps (including heat pumps for cabin comfort cooling and heating in automobiles), mobile air conditioning units (for cooling of passenger compartments in automobiles), dehumidifiers, and combinations thereof. The focus of the present application is air-conditioning and heat pump systems.

[0035] Volumetric capacity is the amount of heat absorbed or rejected divided by the theoretical compressor displacement. Heat removed or absorbed is the enthalpy difference across a heat exchanger multiplied by the refrigerant mass flowrate. Theoretical compressor displacement is the refrigerant mass flowrate divided by the density of the gas entering the compressor (i.e., compressor suction density). More simply, volumetric capacity is the suction density multiplied by the heat exchanger enthalpy difference. Higher volumetric capacity allows the use of a smaller compressor for the same heat load. Herein, cooling capacity refers to the volumetric capacity in cooling mode and heating capacity refers to the volumetric capacity in heating mode.

[0036] Coefficient of performance (COP) is the amount of heat absorbed or rejected divided by the required energy input to operate the cycle (approximated by the compressor power). COP is specific to the mode of operation of a heat pump, thus COP for heating or COP for cooling. COP is directly related to the energy efficiency ratio (EER).

[0037] Subcooling refers to the reduction of the temperature of a liquid below that liquid's saturation point for a given pressure. The liquid saturation point is the temperature at which the vapor is completely condensed to a liquid. By cooling a liquid below the saturation temperature (or bubble point temperature), the net refrigeration effect can be increased. Subcooling thereby improves refrigeration

capacity and energy efficiency of a system. The subcool amount is the amount of cooling below the saturation temperature (in degrees).

[0038] Superheating refers to the increase of the temperature of a vapor above that vapor's saturation point for a given pressure. The vapor saturation point is the temperature at which the liquid is completely evaporated to a vapor. Superheating continues to heat the vapor to a higher temperature vapor at the given pressure. By heating the vapor above the saturation temperature (or dew point temperature), the net refrigeration effect can be increased. Superheating thereby improves refrigeration capacity and energy efficiency of a system when it occurs in the evaporator. Suction line superheat does not add to the net refrigeration effect and can reduce efficiency and capacity. The superheat amount is the amount of heating above the saturation temperature (in degrees).

[0039] Temperature glide (sometimes referred to simply as "glide") is the absolute value of the difference between the starting and ending temperatures of a phase-change process by a refrigerant within a condenser of a refrigerant system, exclusive of any subcooling or superheating. For an evaporator, the glide is the difference in temperature between the dew point and the evaporator inlet. Glide may be used to describe condensation or evaporation of a near azeotrope or non-azeotropic composition. When referring to the temperature glide of an air conditioning or heat pump system, it is common to provide the average temperature glide being the average of the temperature glide in the evaporator and the temperature glide in the condenser. Glide is applicable to blend refrigerants, i.e. refrigerants that are composed of at least 2 components.

[0040] The net refrigeration effect is the quantity of heat that each kilogram of refrigerant absorbs in the evaporator to produce useful cooling.

[0041] The mass flow rate is the quantity of refrigerant in kilograms circulating through the refrigeration, heat pump or air conditioning system over a given period of time.

[0042] As used herein, the term "lubricant" means any material added to a composition or a compressor (and in contact with any heat transfer composition in use within any heat transfer system) that provides hydrodynamic lubrication to the compressor to aid in preventing parts from seizing.

[0043] Global warming potential (GWP) is an index for estimating relative global warming contribution due to atmospheric emission of a kilogram of a particular greenhouse gas compared to emission of a kilogram of carbon dioxide. GWP can be calculated for different time horizons showing the effect of atmospheric lifetime for a given gas. The GWP for the 100-year time horizon is commonly the value referenced. For mixtures, a weighted average can be calculated based on the individual GWPs for each component. Herein, the GWP values are those reported in the United Nations Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4). The GWP of 1252zc is estimated at 1.

[0044] Ozone depletion potential (ODP) is a number that refers to the amount of ozone depletion caused by a substance. The ODP is the ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11 (fluorotrichloromethane). Thus, the ODP of CFC-11 is defined to be 1.0. Other CFCs and HCFCs have ODPs that range from 0.01 to 1.0. Hydrofluorocarbons (HFCs) and the hydrofluoro-olefins (HFO's) described herein have zero ODP because they do not contain chlorine, bromine or iodine, species known to contribute to ozone breakdown and depletion. HFO-1252zc has zero ozone depletion potential.

[0045] 1,1-Difluoropropene (HFO-1252zc or R-1252zc) may be prepared by hydrogenation of 3,3,3-trifluoropropene (HFO-1243zf) over palladium on carbon catalyst to form 1,1,1-trifluoropropane (HFC-263fb), followed by dehydrofluorination of the HFC-263fb over chrome catalyst or by pyrolysis at high temperatures (see attorney docket number FL2084, filed herewith, and herein incorporated by reference).

[0046] E-1,3,3,3-Tetrafluoropropene (HFO-1234zeE or R-1234zeE) is available commercially from Honeywell (Charlotte, North Carolina, USA). And difluoromethane (HFC-32 or R-32) is available commercially from various sources worldwide.

[0047] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may

include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus.

[0048] The transitional phrase "consisting of" excludes any element, step, or ingredient not specified. If in the claim such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consists of" appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

[0049] The transitional phrase "consisting essentially of" is used to define a composition, method or apparatus that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention. The term 'consisting essentially of' occupies a middle ground between “comprising” and 'consisting of'. Typically, components of the refrigerant mixtures and the refrigerant mixtures themselves can contain minor amounts (e.g., less than about 0.5 weight percent total) of impurities and/or byproducts (e.g., from the manufacture of the refrigerant components or reclamation of the refrigerant components from other systems) which do not materially affect the novel and basic characteristics of the refrigerant mixture.

[0050] Also, use of “a” or “an” are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0051] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the disclosed compositions, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety, unless a particular

passage is cited. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

REFRIGERANT COMPOSITIONS

[0052] In one embodiment, compositions comprise, consist of, or consist essentially of HFO-1252zc, HFC-32, and HFO-1234zeE. These compositions provide low Global Warming Potential (GWP), improved environmental fate characteristics, and improved energy efficiency (COP).

[0053] In another embodiment, the compositions comprise, consist of, or consist essentially of from about 0.5 to 65 weight percent HFO-1252zc, from about 21 to 22 weight percent HFC-32, and from about 13 to 78 weight percent HFO-1234zeE.

[0054] Flammability is a term used to mean the ability of a composition to ignite and/or propagate a flame. For refrigerants and other heat transfer compositions or working fluids, the lower flammability limit ("LFL") is the minimum concentration of the heat transfer composition in air that is capable of propagating a flame through a homogeneous mixture of the composition and air under test conditions specified in ASTM (American Society of Testing and Materials) E681. The upper flammability limit ("UFL") is the maximum concentration of the heat transfer composition in air that is capable of propagating a flame through a homogeneous mixture of the composition and air under the same test conditions.

[0055] In order for a refrigerant to be classified by ANSI/ASHRAE as low flammability (class 2L), it must: 1) exhibit flame propagation when tested at 140°F (60°C) and 14.7 psia (101.3 kPa); 2) have an LFL >0.0062 lb/ft^3 (0.10 kg/m^3); 3) have a heat of combustion <8169 Btu/lb (19,000 kJ/kg); and 4) have a maximum burning velocity of ≤3.9 in./s (10 cm/s) when tested at 73.4°F (23.0°C) and 14.7 psia (101.3 kPa) in dry air.

[0056] In order for a refrigerant to be classified by ANSI/ASHRAE as flammable (class 2), it must: 1) exhibit flame propagation when tested at 140°F (60°C) and 14.7 psia (101.3 kPa); 2) have an LFL >0.0062 lb/ft^3 (0.10 kg/m^3); and 3) have a heat of combustion <8169 Btu/lb (19,000 kJ/kg).

[0057] ASHRAE Standard 34 provides a methodology to calculate the heat of combustion for refrigerant blends using a balanced stoichiometric equation based on the complete combustion of one mole of refrigerant with enough oxygen for a stoichiometric reaction.

[0058] HFO-1252zc can be combined with HFC-32 and HFO-1234zeE and provide estimated class 2 or class 2L flammability as defined by ANSI/ASHRAE standard 34 and ISO 817. Class 2 and class 2L flammability may be manageable in refrigeration systems. Specific applications may have different requirements, with regards to flammability.

[0059] The compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE may further comprise at least one additional compound from the list in Table 1.

TABLE 1

Code	Name-ASHRAE Designation	Formula
R-22	chlorodifluoromethane	CHF_2Cl
R-23	trifluoromethane (HFC-23)	CHF_3
R-30	dichloromethane (HCC-30)	CH_2Cl_2
R-31	chlorofluoromethane (HCFC-31)	CH_2FCl
R-40	methyl chloride (HCC-40)	CH_3Cl
R-41	Fluoromethane (HFC-41)	CH_3F
R-50	methane	CH_4
R-125	1,1,2,2,2-pentafluoroenthane (HFC-125)	CF_2CF_3
R-143	1,1,2-trifluoroethane (HFC-143)	CF_2CH_2F
R-143a	1,1,1-trifluoroethane(HFC-143a)	CF_3CH_3
R-152a	1,1,difluoroethane (HFC-152a)	CHF_2CH_3
R-245cb	1,1,1,2,2-pentafluoropropane (HFC-245cb)	$CF_3CF_2CH_3$
R-253dc	2-chloro-1,1,1-trifluoropropane (HCFC-253dc)	$CF_3CHClCH_3$
R-254fb	1,1,1,3-tetrafluoropropane (HFC-254fb)	$CF_3CH_2CH_2F$
R-260fb	1,1,1-trichloropropane (HCC-260fb)	$CCl_3CH_2CH_3$
R-261fc	1,1-dichloro-1-fluoropropane (HCFC-261fc)	$CCl_2FCH_2CH_3$
R-262fc	1-chloro-1,1-difluoropropane (HCFC-262fc)	$CClF_2CH_2CH_3$
R-263fb	1,1,1-trifluoropropane (HFC-263fb)	$CF_3CH_2CH_3$
R-272fb	1,1-difluoropropane (HFC-272fb)	$CHF_2CH_2CH_3$
R-290	propane (HC-290)	$CH_3CH_2CH_3$
R-374	tetrafluorobutene (HFO-374)	$C_4H_6F_4$
R-600	butane (HC-600)	$CH_3CH_2CH_2CH_3$
	allene	$H_2C=C=CH_2$

Code	Name-ASHRAE Designation	Formula
	2-butene	$CC_3CH=CHCH_3$
	cyclobutene	C_4H_6
	2-methylpropene	$CH_3(CH_3)C=CF_3$
R-1122	1-chloro-2,2-difluoroethylene (HCFO-1122)	$CHCl=CF_2$
R-1132	1,2-difluoroethene (HFO-1132)	CHF=CHF
R-1132a	1,1-difluorothene ((HFO-1132a)	$CH=CF_2$
R-1141	fluoroethene (HFO-1141)	$CH_2=CHF$
R-1150	ethylene (HO-1150)	$CH_2=CH_2$
R-1233xf	2-chloro-3,3,3-trifluoropropene (HCFO-1233xf)	$CF_3CCl=CH_2$
R-1234yf	2,3,3,3-tetrafluoropropene(HFO-1234yf)	CF3CH=CHF
R-1242zf	3-chloro-3,3-difluoropropene (HCFO-1242zf)	$CClF_2CH=CH_2$
R-1243zf	3,3,3-trifluoropropene (HFO-1243zf)	$CF_3CH=CH_2$
R-1251	HCFO-1251 isomer	C_3H_4FCl
R-1251	HCFO-1251 isomer	C_3H_4FCl
R-1252ze	1,3-difluoropropene (HFO-1252ze)	$CH_2FCH=CHF$
R-1252yf	2,3-difluoropropene (HFO-1252yf)	$CH_2FCF=CH_2$
R-1252zf	3,3-difluoropropene (HFO-1252zf)	$CHF_2CH=CH_2$
R-1252ye	1,2-difluoropropene (HFO1252ye)	$CH_3CF=CHF$
R-1260zf	3-chloropropene (HCO-1260zf)	$CH_2ClCH=CH_2$
R-1261	3-fluoro-1-propene (HFO-1261)	$CH_2FCH=CH_2$
R-1270	propylene (HO-1270)	$CH_3CH=CH_2$
R-1345	pentafluorobutene (HFO-1345)	$C_4H_3F_5$
	E/Z-*t*-BuO-CF=CH-CH_3	E/Z-t-BuO-CF=CH-CH_3

[0060] In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE may further comprise at least one additional compound selected from HCFC-22, HCC-40, HFO-1234yf, HFO-1243zf, HFO-263fb, HFO-1252ze, HFO-1252yf, HFO-1252zf, and HFO-1252ye. In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE may further comprise at least one additional compound comprising HFO-1234yf. In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE may further comprise at least one additional compound comprising HFO-1243zf. In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE may further comprise at least one additional compound comprising HFO-263fb.

[0061] Some of the compounds present in the compositions of the present invention identified in Table 1 may exist as different configurational isomers or stereoisomers. The present invention is intended to include all single configurational isomers, single stereoisomers or any combination or mixture thereof. For instance, 1,2-difluoroethene (HFO-1132) is meant to represent the cis-isomer (Z), trans-isomer (E), or any combination or mixture of both isomers in any ratio. Single isomers or multiple isomers of the same compound may be used in any proportion.

[0062] The amount of additional compounds present in any of the foregoing refrigerant compositions can be greater than 0 ppm and less than 5,000 ppm and, in particular, can range from greater than zero to about 1,000 ppm, about 5 to about 500 ppm and about 1 to about 100 ppm.

[0063] In one embodiment, the amount of additional compounds present in any of the foregoing refrigerant compositions can be greater than 0 and less than 1 wt% of the refrigerant composition, preferably less than 0.5 weight percent, or more preferably less than 0.1 weight percent.

[0064] The compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE will perform more consistently and be more stable with only minor amounts of water present. Thus, the compositions may further comprise less than 100 ppm (by weight) water, preferably less than 20 ppm (by weight) water, and even more preferably less than 10 ppm (by weight) water.

[0065] Additionally, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE will perform more consistently and be more stable with only minor amounts of oxygen or air present. Therefore, the presently claimed compositions may further comprise less than about 5 volume percent non-adsorbable gases (NAG), preferably less than 3 volume percent NAG, and more preferably less than 1.5 volume percent NAG. Further, the presently claimed compositions, due to the presence of air or NAG, will contain less than 1 volume percent oxygen, preferably less than 0.5 volume percent oxygen, and more preferably less than 0.3 volume percent oxygen.

[0066] In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE may contain a stabilizer. Such stabilizer compounds are intended to be present in a small amount

and prevent decomposition due to the presence of water, air, NAG, or oxygen in a system while in use or while the composition is stored. HFO type refrigerants, due to the presence of a double bond, may be subject to thermal instability and decompose under extreme use, handling or storage situations also. Therefore, there may be advantages to adding stabilizers to HFO type refrigerants. Stabilizers may notably include nitromethane, ascorbic acid, terephthalic acid, azoles such as tolutriazole or benzotriazole, phenolic compounds such as tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-tertbutyl-4-methylphenol, epoxides (possibly fluorinated or perfluorinated alkyl epoxides or alkenyl or aromatic epoxides) such as n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, cyclic monoterpenes, terpenes, such as d-limonene, α-terpinene, β-terpinene, γ-terpinene, α-pinene, or β-pinene, phosphites, phosphates, phosphonates, thiols and lactones. Examples of suitable stabilizers are disclosed in WO2019213004, WO2020222864, and WO2020222865; the disclosures of which are hereby incorporated by reference.

[0067] If the composition does include a stabilizer, it may include any amount from 0.001 wt% up to 1 wt%, preferably from about 0.001 to about 0.5 weight percent, more preferably, from about 0.001 to about 0.3 weight percent of any of the stabilizers listed above.

[0068] In some embodiments, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234ze may contain a tracer compound or tracers. The tracer may comprise two or more tracer compounds. In some embodiments, the tracer is present in the compositions at a total concentration of about 50 parts per million by weight (ppm) to about 1000 ppm, based on the weight of the total composition. In other embodiments, the tracer is present at a total concentration of about 50 ppm to about 500 ppm. Alternatively, the tracer is present at a total concentration of about 100 ppm to about 300 ppm.

[0069] The tracer may be present in compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, HFO-1234zeE in predetermined quantities to allow detection of any dilution, contamination or other alteration of the composition. The presence of certain compounds in the composition may indicate by what method or process one of the components has been produced. The tracer

may also be added to the composition in a specified amount in order to identify the source of the composition. In this manner, detection of infringement on patent rights may be accomplished. The tracers may be refrigerant compounds but are present in the composition at levels that are unlikely to impact performance of the refrigerant component of the composition.

[0070] Tracer compounds may be hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof. Examples of tracer compounds include, but are not limited to HFC-23 (trifluoromethane), HCFC-31 (chlorofluoromethane), HFC-41 (fluoromethane), HFC-161 (fluoroethane), HFC-143a (1,1,1-trifluoroethane), HFC-134a (1,1,1,2-tetrafluoroethane), HFC-125 (pentafluoroethane), HFC-236fa (1,1,1,3,3,3-hexafluoropropane), HFC-236ea (1,1,1,2,3,3-hexafluoropropane), HFC 245cb (1,1,1,2,2-pentafluoropropane), HFC-245fa (1,1,1,3,3-pentafluoropropane) , HFC-254eb (1,1,1,2-tetrafluoropropane), HFC-263fb (1,1,1 trifluoropropane), HFC-272ca (2,2-difluoropropane), HFC-281ea (2-fluoropropane), HFC-281fa (1-fluoropropane), HFC-329p (1,1,1,2,2,3,3,4,4-nonafluorobutane), HFC-329mmz (1,1,1-trifluoro-2-methylpropane), HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane), HFC-338pcc (1,1,2,2,3,3,4,4-octafluorobutane), CFC-12 (dichlorodifluoromethane), CFC-11 (trichlorofluoromethane), CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane), CFC-114a (1,1,-dichloro-1,2,2,2-tetrafluoroethane), HCFC-22 (chlorodifluoromethane), HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane), HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane), HCFC-124a (1-chloro-1,1,2,2-tetrafluoroethane), HCFC-141b (1,1-dichloro-1-fluoroethane), HCFC-142b (1-chloro-1,1-difluoroethane), HCFC-151a (1-chloro-1-fluoroethane), HCFC-244bb (2-chloro-1,1,1,2-tetrafluoropropane), HCC-40 (chloromethane), HFO-1141 (fluoroethene), HCFO-1130 (1,2-dichloroethene), HCFO-1130a (1,1-dichloroethene), HCFO-1131 (1-chloro-2-fluoroethene), HCFO-1122 (2-chloro-1,1-difluoroethene), HFO-1123 (1,1,2-trifluoroethene), HFO-1234ye (1,2,3,3-tetrafluoropropene), HFO-1243zf (3,3,3-trifluoropropene), HFO-1225ye (1,2,3,3,3-pentafluoropropene), HFO-1225zc (1,1,3,3,3-pentafluoropropene), PFC-116 (hexafluoroethane), PFC-C216 (hexafluorocyclopropane), PFC-218 (octafluoropropane), PFC-C318

(octafluorocyclobutane), PFC-1216 (hexafluoroethane), PFC-31-10mc (1,1,1,2,2,3,3,4,4,4-decafluorobutane), PFC-31-10my (1,1,1,2,3,3,3-heptafluoro-2-trifluoromethylpropane), and combinations thereof.

[0071] In another embodiment of the present disclosure, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE further comprise at least one lubricant. Lubricants may be selected from polyol ester, polyvinyl ether, and polyalkylene glycol. Lubricants may also comprise those commonly known as "mineral oils" in the field of compression refrigeration lubrication. Mineral oils comprise paraffins (i.e. straight-chain and branched-carbon-chain, saturated hydrocarbons), naphthenes (i.e. cyclic or ring structure saturated hydrocarbons, which may be paraffins) and aromatics (i.e. unsaturated, cyclic hydrocarbons containing one or more rings characterized by alternating double bonds). Lubricants of the present invention further comprise those commonly known as "synthetic oils" in the field of compression refrigeration lubrication. Synthetic oils comprise alkylaryls (i.e. linear and branched alkyl alkylbenzenes), synthetic paraffins and naphthenes, silicones, and polyalphaolefins. Representative conventional lubricants of the present invention are the commercially available BVM 100 N (paraffinic mineral oil sold by BVA Oils), napthenic mineral oil commercially available under the trademark from Suniso® 3GS and Suniso® 5GS by Crompton Co., naphthenic mineral oil commercially available from Pennzoil under the trademark Sontex® 372LT, naphthenic mineral oil commercially available from Calumet Lubricants under the trademark Calumet® RO-30, linear alkylbenzenes commercially available from Shrieve Chemicals under the trademarks Zerol® 75, Zerol® 150 and Zerol® 500 and branched alkylbenzene, sold by Nippon Oil as HAB 22.

[0072] Lubricants of the present invention further comprise those which have been designed for use with hydrofluorocarbon refrigerants and are miscible with refrigerants of the present invention under compression refrigeration and air-conditioning apparatus' operating conditions. lubricants include, but are not limited to, polyol esters (POEs) such as Castrol® 100 (Castrol, United Kingdom), polyalkylene glycols (PAGs) such as RL-488A from Dow (Dow Chemical, Midland, Mich.), and polyvinyl ethers (PVEs) such as PVE-FVC68D.

[0073] In one particular embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234ze are combined with a PAG lubricant or a PVE lubricant or a POE lubricant for usage in an air-conditioning system or heat pump system.

[0074] In the compositions comprising, consisting of or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE including a lubricant, the lubricant may be present in an amount of less than 80 weight percent of the total composition. The lubricant may further be present in an amount of less than 60 weight percent of the total composition. In other embodiments, the amount of lubricant may be between about 0.1 and 50 weight percent of the total composition. The lubricant may also be between about 0.1 and 20 weight percent of the total composition The lubricant may also be between about 0.1 and 5 weight percent of the total composition.

[0075] In another aspect of the invention, the inventive composition comprising, consisting of or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE is used to introduce lubricant into the air-conditioning or heat pump system as well as or alternatively other additives, such as a) acid scavengers, b) performance enhancers, and c) flame suppressants. In one preferred embodiment, the present compositions comprise an acid scavenger.

[0076] Examples of the acid scavengers that may be included in the present compositions include, but are not limited, the stabilizers and/or the epoxide component of the stabilizers disclosed in U.S. Patent No. 8,535,555 and the acid scavengers disclosed in International Application Publication No. WO 2020/222864, the disclosure of each of which is incorporated herein by reference in its entirety.

[0077] In some embodiments, an acid scavenger may comprise one or more epoxides, one or more amines and/or one or more hindered amines, such as, for example but not limited to, epoxybutane.

[0078] The acid scavenger (e.g., the activated aromatic compound, the siloxane, or both) may be present in any concentration that results in a relatively low total acid number, a relatively low total halides concentration, a relatively low total organic acid concentration, or any combination thereof.

[0079] Preferably the acid scavenger is present at a concentration greater than about 0.0050 wt%, more preferably greater than about 0.05 wt% and even more preferably greater than about 0.1 wt% (e.g. greater than about 0.5 wt%) based on the total weight of the refrigerant composition. The acid scavenger preferably is present in a concentration less than about 5 wt%, less than about 4 wt%, less than about 3 wt%, more preferably less than about 2.5 wt% and most preferably greater than about 2 wt% (e. g. less than about 1.8 wt%) based on the total weight of the refrigerant composition.

[0080] Preferred additives include those described in U.S. Pat. Nos. 5,152,926; 4,755,316, which are hereby incorporated by reference. In particular, the preferred extreme pressure additives include mixtures of (A) tolyltriazole or substituted derivatives thereof, (B) an amine (e.g. Jeffamine M-600) and (C) a third component which is (i) an ethoxylated phosphate ester (e.g. Antara LP-700 type), or (ii) a phosphate alcohol (e.g. ZELEC 3337 type), or (iii) a Zinc dialkyldithiophosphate (e.g. Lubrizol 5139, 5604, 5178, or 5186 type), or (iv) a mercaptobenzothiazole, or (v) a 2,5-dimercapto-1,3,4-triadiaZole derivative (e. g. Curvan 826) or a mixture thereof. Additional examples of additives which may be used are given in U.S. Pat. No. 5,976,399 (Schnur, 5:12-6:51, hereby incorporated by reference).

[0081] Acid number is measured according to ASTM D664-01 in units of mg KOH/g. The total halides concentration, the fluorine ion concentration, and the total organic acid concentration is measured by ion chromatography. Chemical stability of the refrigerant system is measured according to ASHRAE 97: 2007 (RA 2017) “Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use within Refrigerant Systems”. The viscosity of the lubricant is tested at 40°C according to ASTM D-7042.

[0082] Mouli et al. (WO 2008/027595 and WO 2009/042847) teach the use of alkyl silanes as a stabilizer in refrigerant compositions containing fluoroolefins. Phosphates, phosphites, epoxides, and phenolic additives also have been employed in certain refrigerant compositions. These are described for example by Kaneko (U.S. patent application Ser. No. 11/575,256, published as U.S. Publication 2007/0290164) and Singh et al. (U.S. patent application Ser. No. 11/250,219,

published as U.S. Publication 2006/0116310). All of these aforementioned applications are expressly incorporated herein by reference.

[0083] Preferred flame suppressants include the flame retardants described in patent application "Refrigerant compositions containing fluorine substituted olefins CA 2557873 A1" and incorporated by reference, as well as fluorinated products such as HFC-125, HFC-227ea, HFC-236fa, CF_3I, and/or Krytox® lubricants, also incorporated by reference and described in patent application "Refrigerant compositions comprising fluoroolefins and uses thereof WO2009018117A1."

[0084] In one embodiment, as used herein, " Group A Fluorinated Substances" includes any substance that (i) contains at least one fully fluorinated methyl ($–CF_3$) or methylene ($–CF_2–$) carbon atom (without any H/Cl/Br/I attached to it); and (ii) meets the criterion for persistence in soil/sediment and water established in Annex XIII (Section 1.1.1) of the European Union's REACH Regulation (https://reachonline.eu/reach/en/annex-xiii-1-1.1-1.1.1.html as accessed on May 2, 2023) and referenced in the Annex XV Restriction Report dated March 22, 2023, the disclosure of which is hereby incorporated by reference (https://echa.europa.eu/documents/10162/f605d4b5-7c17-7414-8823-b49b9fd43aea as accessed on May 2, 2023). In one embodiment, Group A Fluorinated Substances include, but are not limited to, trifluoroacetic acid (TFA).

[0085] In another embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that has a Henry's Law constant $\leq$ 250 $Pa*m^3/mol$ and contains at least one fully fluorinated methyl ($–CF_3$) or methylene ($–CF_2–$) carbon atom (without any H/Cl/Br/I attached to it). In one embodiment, Group A Fluorinated Substances include, but are not limited to, TFA.

[0086] Thus, according to some embodiments, compositions of the present invention which comprise, consist of, or consist essentially of HFO-1252zc, HFC-32, and HFO-1234zeE are free of or substantially free of Group A Fluorinated Substances, such as TFA. In one embodiment, the phrase "free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by gas chromatography with a flame ionization detector, gas

chromatography with a mass detector by analysis of a gas sample or liquid sample, and/or ion chromatography by analysis of a water sample after bubbling the thermal fluid through water. Such methodologies are well known to those skilled in the art. In one embodiment, the phrase "substantially free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is > 0 wt.% and ≤ 5 wt.%, or > 0 wt.% and ≤ 4 wt.%, or > 0 wt.% and ≤ 3 wt.%, or > 0 wt.% and ≤ 2 wt.%, or > 0 wt.% and ≤ 1 wt.%, and all values and ranges therebetween, when measured by gas chromatographic (GC) techniques, for example gas chromatography (GC) with a flame ionization or electron-capture detector, or GC coupled with a mass detector (gas chromatography/mass spectral (GC/MS) method), by ion chromatograph(IC) or ion chromatography mass spectrometry (IC-MS) techniques, or by high-performance liquid chromatography (HPLC) or high-performance liquid chromatography mass spectrometry (HPLC-MS) techniques. The TFA analytical standard may be used in either gas chromatography or ion chromatography and is available from, for example, Sigma Aldrich.

[0087] Further, in some embodiments, degradation products of such compositions of the present invention which comprise, consist of, or consist essentially of HFO-1252zc, HFC-32, and HFO-1234zeE are free of or substantially free of Group A Fluorinated Substances, such as TFA. In one embodiment, the phrase "free of" as used herein with respect to the formation of Group A Fluorinated Substances by the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques. In one embodiment, the phrase "substantially free of" as used herein with respect to the formation of Group A Fluorinated Substances by the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is > 0% and ≤ 5%, or > 0% and ≤ 4%, or > 0% and ≤ 3%, or > 0% and ≤ 2%, or > 0% and ≤ 1%, and all values and ranges therebetween, when measured

by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques.

METHODS AND SYSTEMS

[0088] The compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE are useful in numerous methods and systems that provide air-conditioning and heating.

[0089] In one embodiment, provided is a method of cooling comprising evaporating a composition comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, HFO-1234zeE in the vicinity of a body to be cooled and thereafter condensing said composition, wherein said cooling is provided by an air-conditioner or heat pump.

[0090] In one embodiment, the air conditioner may be a residential, commercial, or industrial air-conditioning system. These may include, but are not limited to, window, ducted, ductless, packaged terminal, and those exterior to, but connected to the building, such as rooftop systems. The present method may be particularly useful in high ambient temperature regions, due to the high critical temperature of blends containing HFO-1252zc, HFC-32, and HFO-1234zeE.

[0091] In another embodiment, provided is a method of heating comprising evaporating a composition comprising HFO-1252zc, HFC-32, HFO-1234zeE and thereafter condensing said composition in the vicinity of a body to be heated, wherein said heating is provided by a heat pump.

[0092] The presently claimed compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, HFO-1234zeE provide heating and cooling performance with desirable results. These compositions provide cooling and/or heating capacity within 13%, or even within 10% of that for R-454C under similar conditions of operation. Additionally the compositions comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, HFO-1234zeE provide improved COP as compared to R-454C under similar conditions of operation.

[0093] In one embodiment, the heat pump is a residential, light commercial or industrial heat pump system. These may include, but are not limited to, residential heat pumps that provide comfort air-conditioning and heating, hot water heat pumps for heating air (by secondary loop) or for heating water for residential or commercial use, heat pumps for heating manufacturing process equipment, and high temperature heat pumps. Due to the high critical temperature of blends containing HFO-1252zc, HFC-32, and HFO-1234zeE it is possible to heat water to higher temperatures than propane or R-454C.

[0094] In another embodiment, the method for producing cooling is particularly useful in regions where the ambient temperature can exceed at least 35ºC.

[0095] In geographic areas with high ambient temperatures, where air conditioning becomes essential, refrigerant compositions with high critical temperatures and high thermal stability are desirable. Currently available hydrofluorocarbon (HFC) refrigerants such as R-410A, R-407C or R-32 have relatively low critical temperatures. As a consequence, these refrigerants do not perform well in extreme hot environments. The energy efficiency of a refrigerant generally decreases as the condensing temperature approaches the refrigerant critical temperature during operation at high ambient temperatures. In hot climates, R-22 has remained the refrigerant of choice for much air conditioning and refrigeration applications as it is not flammable and has a higher critical temperature so that it delivers higher cooling capacity and higher energy efficiency in hot climates as compared to R-410A or R-32. However, R-22 is an ozone depleting substance in the Montreal Protocol to reduce ozone depletion. As such, R-22 has been mandated and legislated for phase out for manufacture for and use in air conditioning and refrigeration. There is interest in finding a refrigerant with the lowest possible direct GWP and also that performs well in hot climate (or high ambient) temperature regions.

[0096] In the method for producing cooling the body to be cooled may be defined as any space, location, object, or body for which it is desirable to provide cooling. Examples include spaces, open or enclosed, that require cooling such as a residence, such as an apartment or apartment building, university dormitory, townhouse or other attached house, or a single-family home; or the body to be

cooled may be any other building, such as an office building, supermarket, college or university classroom or administration buildings.

[0097] In another embodiment, a method for producing air conditioning in high ambient temperatures is provided. The method comprises evaporating a composition comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE and thereafter condensing said composition. The method is particularly useful in regions where ambient temperatures can exceed 35ºC or more.

[0098] In another embodiment, a method is provided for replacing HCFC-22 in high ambient air conditioning apparatus comprising providing a composition comprising, consisting essentially of, or consisting of HFO-1252zc, HFC-32, and HFO-1234zeE to said apparatus. The method of replacing HCFC-22 is particularly useful in regions where ambient temperatures can exceed 35ºC or more.

[0099] Similarly, in some industrial air conditioning applications heat must be released in high ambient temperature environments. HCFC-124 has been used as the working fluid in such applications. HCFC-124 is also controlled under the Montreal protocol as an ozone depleting substance and more environmentally sustainable replacements are desirable. Thus, a method is provided for replacing HCFC-124 in industrial air conditioning apparatus, comprising providing a composition comprising, consisting essentially of, or consisting of HFO-1252zc, HFC-32, and HFO-1234zeE to said apparatus. The method of replacing HCFC-124 is particularly useful in regions where ambient temperatures can exceed 35ºC or more.

[0100] In another embodiment, the method for producing cooling and method for replacing HCFC-22 or HCFC-124 are useful for systems operating in ambient temperatures of 40ºC or higher. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures of 45ºC or higher. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures of 50ºC or higher. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures of 55ºC or higher. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures of 60ºC or higher. In

another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 35-50ºC. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 35-60ºC. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 40- 60ºC. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 45-60ºC. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 50-60ºC.

[0101] In another embodiment, is provided a system for cooling or heating comprising a composition comprising HFO-1252zc, HFC-32, and HFO-1234zeE and optionally a lubricant. The system comprises an evaporator, compressor, condenser, and expansion device, each operably connected to perform a vapor compression cycle.

[0102] The air-conditioner or heat pump system may be a residential, light commercial, or industrial air-conditioner or heat pump. Various such systems are described previously herein.

[0103] In another embodiment, the air-conditioning or heat pump system containing a composition comprising, consisting of, or consisting essentially of HFO-1252zc, HFC-32, and HFO-1234zeE may be a secondary loop system.

[0104] The following Example are provided to illustrate certain aspects of the invention and shall not limit the scope of the appended claims.

EXAMPLES

Example 1

[0105] The presently claimed compositions were compared to R-454C (ASHRAE designation for a refrigerant containing 78.5 wt% HFO-1234yf and 21.5 wt% HFC-32) under the conditions for a residential heat pump shown below. Table 2 provides the calculated results.

Conditions:
T_condenser = 35.0ºC
T_evaporator = -5.0ºC
subcool = 11.1 K
superheat = 8.33 K
compressor efficiency = 0.7
Average Heat Exchanger Temperature Set Points
100 % of superheat is included in refrigeration effect.
Vapor Molar Quality Entering Evaporator: q_4
cooling load = 3.517 kW
compressor displacement = 0.1 (m^3 / min)

TABLE 2

Composition (wt fraction)			T_bp (degC)	T_c (degC)	T_disch (degC)	avg glide (K)	GWP AR5	COP cool (rel)	CAP cool (rel)	COP heat (rel)	CAP heat (rel)
R1252zc	R1234zeE	R32									
0.01	0.78	0.21	-41.2	103	68.0	10.61	143	1.02	0.82	1.02	0.81
0.02	0.77	0.21	-41.23	103	68.1	10.52	143	1.02	0.82	1.02	0.81
0.03	0.76	0.21	-41.26	103	68.1	10.42	143	1.02	0.82	1.02	0.82
0.04	0.75	0.21	-41.29	103	68.2	10.33	143	1.02	0.82	1.02	0.82
0.05	0.74	0.21	-41.31	103	68.2	10.24	143	1.02	0.82	1.02	0.82
0.06	0.73	0.21	-41.34	102	68.2	10.14	143	1.02	0.83	1.02	0.82
0.07	0.72	0.21	-41.36	102	68.3	10.05	143	1.02	0.83	1.02	0.83
0.08	0.71	0.21	-41.38	102	68.3	9.95	143	1.02	0.83	1.02	0.83
0.09	0.70	0.21	-41.41	102	68.3	9.86	143	1.02	0.83	1.02	0.83
0.10	0.69	0.21	-41.42	102	68.4	9.76	143	1.02	0.83	1.02	0.83
0.11	0.68	0.21	-41.44	101	68.4	9.67	143	1.02	0.84	1.02	0.83
0.12	0.67	0.21	-41.46	101	68.5	9.57	143	1.02	0.84	1.02	0.83
0.13	0.66	0.21	-41.47	101	68.5	9.48	143	1.02	0.84	1.02	0.84
0.14	0.65	0.21	-41.49	101	68.5	9.38	143	1.02	0.84	1.02	0.84
0.15	0.64	0.21	-41.5	101	68.6	9.29	143	1.02	0.84	1.02	0.84
0.16	0.63	0.21	-41.51	101	68.6	9.20	143	1.02	0.84	1.02	0.84
0.17	0.62	0.21	-41.52	101	68.6	9.11	143	1.02	0.85	1.02	0.84
0.18	0.61	0.21	-41.53	100	68.7	9.02	143	1.02	0.85	1.01	0.84
0.19	0.60	0.21	-41.54	100	68.7	8.92	143	1.02	0.85	1.01	0.85
0.20	0.59	0.21	-41.55	100	68.7	8.83	143	1.02	0.85	1.01	0.85
0.21	0.58	0.21	-41.56	100	68.8	8.75	143	1.02	0.85	1.01	0.85
0.22	0.57	0.21	-41.57	100	68.8	8.66	143	1.02	0.85	1.01	0.85
0.23	0.56	0.21	-41.57	100	68.9	8.57	143	1.02	0.86	1.01	0.85
0.005	0.7761	0.2189	-41.53	103	68.5	10.73	149	1.02	0.83	1.02	0.82
0.01	0.77	0.22	-41.58	103	68.5	10.68	150	1.02	0.83	1.02	0.83
0.02	0.76	0.22	-41.61	103	68.6	10.59	150	1.02	0.83	1.02	0.83
0.03	0.75	0.22	-41.64	103	68.6	10.49	150	1.02	0.83	1.02	0.83
0.04	0.74	0.22	-41.67	102	68.6	10.39	150	1.02	0.84	1.02	0.83

Composition (wt fraction)			T_bp (degC)	T_c (degC)	T_disch (degC)	avg glide (K)	GWP AR5	COP cool (rel)	CAP cool (rel)	COP heat (rel)	CAP heat (rel)
R1252zc	R1234zeE	R32									
0.05	0.73	0.22	-41.69	102	68.7	10.30	150	1.02	0.84	1.02	0.83
0.06	0.72	0.22	-41.72	102	68.7	10.20	150	1.02	0.84	1.02	0.84
0.07	0.71	0.22	-41.74	102	68.7	10.11	150	1.02	0.84	1.02	0.84
0.08	0.70	0.22	-41.76	102	68.8	10.01	150	1.02	0.84	1.02	0.84
0.09	0.69	0.22	-41.78	101	68.8	9.91	150	1.02	0.85	1.02	0.84
0.10	0.68	0.22	-41.79	101	68.9	9.82	150	1.02	0.85	1.02	0.84
0.11	0.67	0.22	-41.81	101	68.9	9.72	150	1.02	0.85	1.02	0.85
0.12	0.66	0.22	-41.83	101	68.9	9.63	150	1.02	0.85	1.02	0.85
0.13	0.65	0.22	-41.84	101	69.0	9.53	150	1.02	0.85	1.02	0.85
0.14	0.64	0.22	-41.85	101	69.0	9.44	150	1.02	0.85	1.02	0.85
0.15	0.63	0.22	-41.86	100	69.0	9.34	150	1.02	0.86	1.01	0.85
0.16	0.62	0.22	-41.87	100	69.1	9.25	150	1.02	0.86	1.01	0.85
0.17	0.61	0.22	-41.88	100	69.1	9.16	150	1.02	0.86	1.01	0.86
0.18	0.60	0.22	-41.89	100	69.1	9.06	150	1.02	0.86	1.01	0.86
0.19	0.59	0.22	-41.9	100	69.2	8.97	150	1.02	0.86	1.01	0.86
0.20	0.58	0.22	-41.91	100	69.2	8.88	150	1.02	0.86	1.01	0.86
0.21	0.57	0.22	-41.92	100	69.2	8.79	150	1.02	0.87	1.01	0.86
0.22	0.56	0.22	-41.92	100	69.3	8.70	150	1.02	0.87	1.01	0.86
0.23	0.55	0.22	-41.93	100	69.3	8.62	150	1.02	0.87	1.01	0.87
0.24	0.55	0.21	-41.58	100	68.9	8.48	143	1.02	0.86	1.01	0.85
0.25	0.54	0.21	-41.58	100	68.9	8.40	143	1.02	0.86	1.01	0.86
0.26	0.53	0.21	-41.59	100	69.0	8.31	143	1.02	0.86	1.01	0.86
0.27	0.52	0.21	-41.59	100	69.0	8.23	143	1.02	0.86	1.01	0.86
0.28	0.51	0.21	-41.59	99	69.1	8.15	143	1.02	0.86	1.01	0.86
0.29	0.50	0.21	-41.6	99	69.1	8.07	143	1.02	0.86	1.01	0.86
0.30	0.49	0.21	-41.6	99	69.2	7.99	143	1.02	0.86	1.01	0.86
0.31	0.48	0.21	-41.6	99	69.2	7.91	143	1.02	0.87	1.01	0.86
0.32	0.47	0.21	-41.6	99	69.2	7.83	143	1.02	0.87	1.01	0.86
0.33	0.46	0.21	-41.6	99	69.3	7.75	143	1.02	0.87	1.01	0.87
0.34	0.45	0.21	-41.6	99	69.3	7.68	143	1.02	0.87	1.01	0.87
0.35	0.44	0.21	-41.6	99	69.4	7.60	143	1.02	0.87	1.01	0.87
0.36	0.43	0.21	-41.6	99	69.4	7.53	143	1.02	0.87	1.01	0.87
0.37	0.42	0.21	-41.6	99	69.5	7.46	143	1.02	0.87	1.01	0.87
0.38	0.41	0.21	-41.6	99	69.5	7.39	143	1.02	0.87	1.01	0.87
0.39	0.40	0.21	-41.6	99	69.6	7.32	143	1.02	0.87	1.01	0.87
0.40	0.39	0.21	-41.6	99	69.6	7.25	143	1.02	0.88	1.01	0.87
0.41	0.38	0.21	-41.59	99	69.7	7.19	143	1.02	0.88	1.01	0.87
0.42	0.37	0.21	-41.59	98	69.7	7.12	143	1.02	0.88	1.01	0.87
0.43	0.36	0.21	-41.59	98	69.8	7.06	143	1.02	0.88	1.01	0.88
0.44	0.35	0.21	-41.58	98	69.9	7.00	143	1.02	0.88	1.01	0.88
0.45	0.34	0.21	-41.58	98	69.9	6.93	143	1.02	0.88	1.01	0.88
0.46	0.33	0.21	-41.58	98	70.0	6.88	143	1.02	0.88	1.01	0.88
0.47	0.32	0.21	-41.57	98	70.0	6.82	143	1.02	0.88	1.01	0.88
0.48	0.31	0.21	-41.57	98	70.1	6.76	143	1.02	0.88	1.01	0.88

Composition (wt fraction)			T_bp (degC)	T_c (degC)	T_disch (degC)	avg glide (K)	GWP AR5	COP cool (rel)	CAP cool (rel)	COP heat (rel)	CAP heat (rel)
R1252zc	R1234zeE	R32									
0.49	0.30	0.21	-41.57	98	70.2	6.70	143	1.02	0.88	1.01	0.88
0.50	0.29	0.21	-41.56	98	70.2	6.65	143	1.02	0.88	1.01	0.88
0.51	0.28	0.21	-41.56	98	70.3	6.60	143	1.02	0.88	1.01	0.88
0.52	0.27	0.21	-41.55	98	70.4	6.55	143	1.02	0.89	1.01	0.88
0.53	0.26	0.21	-41.55	98	70.5	6.50	143	1.02	0.89	1.01	0.88
0.54	0.25	0.21	-41.54	98	70.5	6.45	143	1.02	0.89	1.01	0.88
0.55	0.24	0.21	-41.54	98	70.6	6.40	143	1.02	0.89	1.01	0.88
0.56	0.23	0.21	-41.54	98	70.7	6.36	143	1.02	0.89	1.01	0.88
0.57	0.22	0.21	-41.53	98	70.8	6.31	143	1.02	0.89	1.01	0.89
0.58	0.21	0.21	-41.53	98	70.8	6.27	143	1.02	0.89	1.01	0.89
0.59	0.20	0.21	-41.52	98	70.9	6.23	143	1.02	0.89	1.01	0.89
0.60	0.19	0.21	-41.52	98	71.0	6.19	143	1.02	0.89	1.01	0.89
0.61	0.18	0.21	-41.51	98	71.1	6.15	143	1.02	0.89	1.01	0.89
0.62	0.17	0.21	-41.51	98	71.2	6.12	143	1.02	0.89	1.01	0.89
0.63	0.16	0.21	-41.5	98	71.3	6.08	143	1.02	0.89	1.01	0.89
0.64	0.15	0.21	-41.5	98	71.4	6.05	143	1.02	0.89	1.01	0.89
0.24	0.54	0.22	-41.93	99	69.4	8.53	150	1.02	0.87	1.01	0.87
0.25	0.53	0.22	-41.94	99	69.4	8.45	150	1.02	0.87	1.01	0.87
0.26	0.52	0.22	-41.94	99	69.4	8.36	150	1.02	0.87	1.01	0.87
0.27	0.51	0.22	-41.94	99	69.5	8.28	150	1.02	0.87	1.01	0.87
0.28	0.50	0.22	-41.94	99	69.5	8.20	150	1.02	0.87	1.01	0.87
0.29	0.49	0.22	-41.95	99	69.6	8.11	150	1.02	0.88	1.01	0.87
0.30	0.48	0.22	-41.95	99	69.6	8.03	150	1.02	0.88	1.01	0.87
0.31	0.47	0.22	-41.95	99	69.7	7.96	150	1.02	0.88	1.01	0.88
0.32	0.46	0.22	-41.95	99	69.7	7.88	150	1.02	0.88	1.01	0.88
0.33	0.45	0.22	-41.95	99	69.7	7.80	150	1.02	0.88	1.01	0.88
0.34	0.44	0.22	-41.95	99	69.8	7.73	150	1.02	0.88	1.01	0.88
0.35	0.43	0.22	-41.95	98	69.8	7.65	150	1.02	0.88	1.01	0.88
0.36	0.42	0.22	-41.95	98	69.9	7.58	150	1.02	0.88	1.01	0.88
0.37	0.41	0.22	-41.94	98	69.9	7.51	150	1.02	0.88	1.01	0.88
0.38	0.40	0.22	-41.94	98	70.0	7.44	150	1.02	0.89	1.01	0.88
0.39	0.39	0.22	-41.94	98	70.0	7.37	150	1.02	0.89	1.01	0.88
0.40	0.38	0.22	-41.94	98	70.1	7.30	150	1.02	0.89	1.01	0.88
0.41	0.37	0.22	-41.94	98	70.2	7.24	150	1.02	0.89	1.01	0.89
0.42	0.36	0.22	-41.93	98	70.2	7.17	150	1.02	0.89	1.01	0.89
0.43	0.35	0.22	-41.93	98	70.3	7.11	150	1.02	0.89	1.01	0.89
0.44	0.34	0.22	-41.93	98	70.3	7.05	150	1.02	0.89	1.01	0.89
0.45	0.33	0.22	-41.92	98	70.4	6.99	150	1.02	0.89	1.01	0.89
0.46	0.32	0.22	-41.92	98	70.4	6.93	150	1.02	0.89	1.01	0.89
0.47	0.31	0.22	-41.91	98	70.5	6.87	150	1.02	0.89	1.01	0.89
0.48	0.30	0.22	-41.91	98	70.6	6.82	150	1.02	0.89	1.01	0.89
0.49	0.29	0.22	-41.9	98	70.6	6.76	150	1.02	0.89	1.01	0.89
0.50	0.28	0.22	-41.9	98	70.7	6.71	150	1.02	0.90	1.01	0.89
0.51	0.27	0.22	-41.9	98	70.8	6.66	150	1.02	0.90	1.01	0.89

Composition (wt fraction)			T_bp (degC)	T_c (degC)	T_disch (degC)	avg glide (K)	GWP AR5	COP cool (rel)	CAP cool (rel)	COP heat (rel)	CAP heat (rel)
R1252zc	R1234zeE	R32									
0.52	0.26	0.22	-41.89	98	70.9	6.61	150	1.02	0.90	1.01	0.89
0.53	0.25	0.22	-41.89	98	70.9	6.56	150	1.02	0.90	1.01	0.89
0.54	0.24	0.22	-41.88	98	71.0	6.51	150	1.02	0.90	1.01	0.90
0.55	0.23	0.22	-41.88	98	71.1	6.47	150	1.02	0.90	1.01	0.90
0.56	0.22	0.22	-41.87	98	71.2	6.42	150	1.02	0.90	1.01	0.90
0.57	0.21	0.22	-41.87	98	71.2	6.38	150	1.02	0.90	1.01	0.90
0.58	0.20	0.22	-41.86	98	71.3	6.34	150	1.02	0.90	1.01	0.90
0.59	0.19	0.22	-41.85	98	71.4	6.30	150	1.02	0.90	1.01	0.90
0.60	0.18	0.22	-41.85	98	71.5	6.26	150	1.02	0.90	1.01	0.90
0.61	0.17	0.22	-41.84	98	71.6	6.22	150	1.02	0.90	1.01	0.90
0.62	0.16	0.22	-41.84	98	71.7	6.19	150	1.02	0.90	1.01	0.90
0.63	0.15	0.22	-41.83	98	71.8	6.16	150	1.02	0.90	1.01	0.90
0.64	0.14	0.22	-41.83	98	71.9	6.12	150	1.02	0.90	1.01	0.90
0.65	0.13	0.22	-41.82	98	72.0	6.09	150	1.02	0.90	1.01	0.90

[0106] The data demonstrates that compositions comprising HFO-1252zc, HFC-32, and HFO-1234zeE provide higher COP (a measure of energy efficiency) than either propane or R-454C, in both cooling and heating mode. Additionally, cooling and heating capacity is within 13% or even 10% of that for R-454C. Therefore, the present inventive compositions provide reasonable replacements for R-454C.

Example 2

[0107] The presently claimed compositions were compared to R-454C (ASHRAE designation for a refrigerant containing 78.5 wt% HFO-1234yf and 21.5 wt% HFC-32) under the conditions for residential air conditioning shown below. Table 3 provides the calculated results under the following conditions.

Average condenser temp = 46.1°C [115°F],

Average evaporator temp = 10.0°C [50°F],

Subcool = 8.3 K [15°F],

Superheat = 11.1 K [20°F],

Compressor efficiency = 0.70

TABLE 3

Composition	GWP, AR4 (AR5)	BP, °C	Cooling Capacity (rel to R-454C)	COP for cooling (rel to R-454C)	Average Glide, K	Compressor Discharge Temp, °C
R-454C	148 (146)	-45.6	1.00	1.00	6.3	73.2
1252zc/R32/1234zeE (30/21/49 wt%)	145 (143)	-41.6	0.90	1.04	7.6	78.4
propane	0 (1)	-42.1	0.88	1.03	0	68.5

[0108] The inventive composition containing HFO-1252zc, HFC-32, and HFO-1234zeE provides similar capacity to R-454C (within 10%), which is higher than for propane. Further, the composition provides improved COP relative to R-454C and slightly better than propane as well. All of this while maintaining GWP less than 150 and reasonable average temperature glide.

CLAIMS

What is claimed is:

1. A composition comprising HFO-1252zc, HFC-32, and HFO-1234zeE.

2. The composition of claim 1 comprising from about 0.5 to 65 weight percent HFO-1252zc, from about 21 to 22 weight percent HFC-32, and from about 13 to 78 weight percent HFO-1234zeE.

3. The composition of claim 1 comprising about 30 weight percent HFO-1252zc, about 21 weight percent HFC-32, and about 49 weight percent HFO-1234zeE.

4. The composition of any of claims 1 to 3, further comprising at least one additional compound selected from HCFC-22, HFC-23, HCC-30, HCFC-31, HCC-40, HFC-41, methane, HFC-125, HFC-143, HFC-143a, HFC-152a, HFC-245cb, HCFC-253dc, HFC-254fb, HCC-260fb, HCFC-261fc, HCFC-262fc, HFC-263fb, HFC-272fb, propane, HFO-374, n-butane, allene, 2-butene, cyclobutene, 2-methyl propene, HCFO-1122, HFO-1132, HFO-1132a, HFO-1141, ethylene, HCFO-1233xf, HFO-1234yf, HCFO-1242zf, HFO-1243zf, HCFO-1251, HCO-1260zf, HFO-1261zf, propylene, HFO-1345, HFO-1252ze, HFO-1252yf, HFO-1252zf, HFO-1252ye, and E/Z-t-BuO-CF=CH-CH_3.

5. The composition of any of claims 1 to 4, further comprising at least one additional compound selected from HCFC-22, HCC-40, HFO-1234yf, HFO-1243zf, HFC-263fb, HFO-1252ze, HFO-1252yf, HFO-1252zf, and HFO-1252ye.

6. The composition of any of claims 1 to 5, wherein said composition further comprises from 0.1 to 200 ppm by weight of water; from about 10 ppm by volume to about 0.35 volume percent oxygen; and/or from about 100 ppm by volume to about 1.5 volume percent air or NAG.

7. The composition of any of claims 1 to 3, wherein said composition comprises a stabilizer.

8. The composition of claim 7, wherein the stablilizer is selected from the group consisting of nitromethane, ascorbic acid, terephthalic acid, azoles, phenolic compounds, cyclic monoterpenes, terpenes, phosphites, phosphates, phosphonates, thiols, and lactones.

9. The composition of any of claims 7 or 8, wherein the stabilizer is selected from tolutriazole, benzotriazole, tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-terbutyl-4-methylphenol, fluorinated epoxides, n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, d-limonene, α-terpinene, β-terpinene, α-pinene, β-pinene, or butylated hydroxytoluene.

10. The composition of any of claims 7 to 9, wherein the stabilizer is present in an amount from about 0.001 to 1.0 weight percent based on the weight of the refrigerant.

11. The composition of any of claims 1 to 10, wherein the composition further comprises a lubricant.

12. The composition of claim 11, wherein said lubricant is at least one selected from the group consisting of polyalkylene glycol, polyol ester, poly-α-olefin, and polyvinyl ether.

13. The composition of claim 11 or 12, wherein said lubricant is a polyol ester or a polyvinyl ether.

14. The composition of any of claims 11 to 13, wherein said lubricant has at least one property selected from the group consisting of volume resistivity of greater than 10^{10} Ω-m at 20 ºC; surface tension of from about 0.02 N/m to 0.04 N/m at 20 ºC; kinematic viscosity of from about 20 cSt to about 500 cSt at 40 ºC; a breakdown voltage of at least 25 kV; and a hydroxy value of at most 0.1 mg KOH/g.

15. The composition of any of claims 1 to 14, wherein the composition comprises at least one tracer.

16. The composition of claim 15, wherein said tracer is present in an amount from about 1.0 ppm by weight to about 1000 ppm by weight.

17. The composition of any of claims 15 or 16, wherein said at least one tracer is selected from the group consisting of hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins,

chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof.

18. The composition of any of claims 15 to 17, wherein said at least one tracer is selected from the group consisting of HFC-23, HCFC-31, HFC-41, HFC-161, HFC-143a, HFC-134a, HFC-125, HFC-236fa, HFC-236ea, HFC-245cb, HFC-245fa, HFC-254eb, HFC-263fb, HFC-272ca, HFC-281ea, HFC-281fa, HFC-329p, HFC-329mmz, HFC338mf, HFC-338pcc, CFC-12, CFC-11, CFC-114, CFC-114a, HCFC-22, HCFC-123, HCFC-124, HCFC-124a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-244bb, HCC-40, HFO-1141, HCFO-1130, HCFO-1130a, HCFO-1131, HCFO-1122, HFO-1123, HFO-1234yf, HFO-1234ye, HFO-1243zf, HFO-1225ye, HFO-1225zc, PFC-116, PFC-C216, PFC-218, PFC-C318, PFC-1216, PFC-31-10mc, PFC-31-10my, and combinations thereof.

19. The composition of any of claims 1 or 18, wherein the composition is free of or substantially free of Group A Fluorinated Substances, and wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.

20. A method for cooling comprising evaporating a composition of any of claims 1 to 19 in the vicinity of a body to be cooled and thereafter condensing said composition, wherein said cooling is provided by an air-conditioner or heat pump.

21. A method for heating comprising evaporating a composition of any of claims 1 to 19 and thereafter condensing said composition in the vicinity of a body to be heated, wherein said heating is provided by a heat pump.

22. A system for cooling or heating comprising a composition of any of claims 1 to 19.

23. The system of claim 22, comprising an evaporator, compressor, condenser, and expansion device, each operably connected to perform a vapor compression cycle.

24. The system of claim 22 or 23, wherein said air-conditioner or heat pump is a residential, light commercial, or industrial air-conditioner or heat pump.

25. A method of replacing R-454C or propane in air-conditioning or heat pump systems comprising providing the composition of any of claims 1 to 19 to the system in place of R-454C or propane.

26. Use of the composition of any of claims 1 to 19 as refrigerant in air-conditioning or heat pump systems.

27, The system of any of claims 22 to 24, wherein said system is a secondary loop system.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/037124

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K5/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2012/126187 A1 (LOW ROBERT E [GB]) 24 May 2012 (2012-05-24) paragraphs [0001] - [0017], [0069] - [0070]; claims -----	1-24,26, 27 25

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 September 2024	01/10/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Martinez Marcos, V

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/037124

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012126187 A1	24-05-2012	AU 2010238362 A1	03-11-2011
		BR PI1015017 A2	12-04-2016
		CA 2758412 A1	21-10-2010
		CN 102428129 A	25-04-2012
		EP 2440607 A1	18-04-2012
		ES 2536649 T3	27-05-2015
		HK 1168616 A1	04-01-2013
		JP 5687688 B2	18-03-2015
		JP 2012524137 A	11-10-2012
		KR 20120025472 A	15-03-2012
		RU 2011146318 A	27-05-2013
		US 2012126187 A1	24-05-2012
		WO 2010119265 A1	21-10-2010
		ZA 201107349 B	24-06-2015